K.A. Romanova [1]
Yu.G.Galyametdinov [1]

THE INFLUENCE OF LEWIS BASES ON THE LIQUID-CRYSTALLINE AND PHOTOPHYSICAL PROPERTIES OF LANTHANIDE(III) COMPLEXES

[1]Physical and Colloid Chemistry Department, Kazan National Research Technological University, Karl Marx Str., 68, Kazan, Russia

ksenuya@mail.ru

Lanthanide (Ln) complexes have a great potential as materials for optoelectronic devices, organic light emitting diodes, flat and flexible displays, luminescent biological probes and solar batteries. Mesogenic Ln(III) complexes can self-organize into liquid-crystalline mesophase and form optically transparent films with polarized luminescence, whose intensity can be controlled by magnetic field, temperature, and laser irradiation. Their photophysical properties are mainly defined by the ligand environment [1]. In this study, the influence of the Lewis base structure on the molecular anisotropy and photophysical properties of some mesogenic Ln(III) complexes was inverstigated. Quantum-chemical calculations were used to evaluate the influence of the Lewis base structure on the anisometry of Ln(III) complexes molecules and on their subsequent supramolecular organization.

Theoretical simulation of equilibrium geometries of Ln(III) complexes was performed in the gas phase by the DFT method with the PBE functional. The energies of the lowest singlet and triplet excited states were found by TDDFT method (functionals PBE, B3LYP) in program Firefly 8. For Ln(III) ions the scalar relativistic 4f-in-core pseudopotentials (ECPs) with the associated valence basis sets were used and 6-31G(d,p) basis set - for other atoms. Absorption spectra were simulated using SMLC model in ORCA 3.0.3 program.

Quantum-chemical simulation of Ln(III) complexes also makes it possible to foresee and afterward to synthesize compounds with liquid-crystalline properties. Such a prediction can be made on the basis of the value of geometric anisotropy, i.e. the ratio of the long inertial axis of a molecule to its short inertial axis in the ellipsoid of revolution. Though this value for the majority of known organic liquid crystals lies in the range from 4 to 8, it reaches values of 1.6 - 1.8 in case of europium(III) complexes with 1,10-phenanthroline and 2.5 - 3.5 with 2,2'-bipyridine. On the basis of the calculated excited states the main intramolecular energy transfer channels were determined. Good agreement between simulated and experimental data showed that the proposed methodology allows to predict the photophysical properties of Ln(III) complexes and can be used to describe intramolecular energy transfer processes. According to the quantum-chemical calculations the revealed structural features of the studied compounds can predetermine their effective luminescence in self-organized films and their application as phosphorescent emitters.

The calculations were performed using the facilities of the Joint Supercomputer Center of Russian Academy of Sciences and the Supercomputing Center of Lomonosov, Moscow State University [2].

1. Romanova K.A. et al. *Journal of Physical Chemistry A*, 2014, **118**: 11244-11252.
2. Voevodin V.V. et al. *Open Systems Journal*, 2012, **7**: 36-39.

This work was supported by the grant of the President of the Russian Federation for the state support of the young Russian scientists - candidates of sciences (No MK-7320.2016.3).